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STRESSED-OXIDATION LIFETIME OF DIFFERENT SiC FIBER, CVI MATRIX SiC MINICOMPOSITES IN AIR

Gregory N. MORSCHER

Case Western Reserve University*, Cleveland Ohio, USA

Julian MARTINEZ-FERNANDEZ

University of Seville, Seville, Spain

The stressed-oxidation lifetime properties of several minicomposites composed of single fiber tows with a CVI SiC matrix were compared. The minicomposites were made up of Nicalon™ and Hi-Nicalon™ SiC fibers with carbon or BN interphases. Constant load stress-rupture tests were performed between 600 and 1300°C in air for all of the minicomposite systems. Cyclic load testing was performed on the Hi-Nicalon minicomposite systems. The factors controlling the different lifetime behaviors: fiber rupture properties, interphase oxidation, fiber degradation, and fiber-matrix bonding, are discussed in light of different minicomposite constituents. All of the systems were subject to intermediate temperature embrittlement. The Hi-Nicalon fiber, BN interphase system, performed the best for constant load conditions. For cyclic load conditions, both the BN-interphase and C-interphase minicomposites displayed poor, but different failure behavior.

1. INTRODUCTION

Predicting the useful life of ceramic fiber reinforced ceramic matrix composites (CMC's) necessitates the understanding of the factors controlling the time to failure of a CMC at elevated temperatures in oxidizing environments for different stresses. The high temperature load carrying ability of CMC's will ultimately depend on the load carrying ability of the reinforcing fibers. Several factors can lead to the loss of load carrying ability in a CMC:

i. *Intrinsic fiber creep-rupture mechanisms¹*

* Resident Research Associate at NASA Lewis Research Center, MS 106-5, Cleveland, OH 44135 USA

- ii. *Extrinsic, environmentally assisted slow crack growth or creep-rupture mechanisms.* For example, an oxide scale which forms on a fiber surface can act as a large flaw^{2,3} at temperatures too low for creep mechanisms to operate. In addition, such a scale results in loss of cross-sectional area at elevated temperatures and increased stress on the fiber in the creep-rupture controlled regime.
- iii. *Volatilization of the interphase resulting in longer maximum load-bearing gage lengths for reinforcing fibers⁴.*
- iv. *Environmentally assisted creation of new flaws on the fiber surface due to a change in fiber surface conditions after composite processing.* For example, the surface of Nicalon^{TM**} fibers undergoes changes during long time exposure at 1000°C resulting in C and SiO₂ layers formed on the fiber surface⁵. This fiber surface alteration was believed to result in minor strength degradation for CVI SiC composites⁵ due to the long-time thermal exposure during CVI SiC processing. However, it is possible that this change in the fiber surface morphology led to the severe degradation in load carrying ability for Nicalon/C-interphase/CVI SiC minicomposites at 700°C⁶ in air where the fibers were exposed to O₂ after the C-interphase had volatilized.
- v. *Fiber fusing to matrix due to the reaction products formed from reactions of the environment with the interphase, fiber, and matrix.* A strong bond formed between the fiber and matrix can lead to large stress-concentrations on the fibers⁷ if the applied loading on the fibers fluctuates. This is considered to be the case for the severe loss in load carrying ability of BN interphase, Hi-Nicalon^{TM**}, CVI SiC matrix minicomposites when subjected to low cycle fatigue at intermediate temperatures⁸.

The approach of this study was to compare the time to failure of single tow minicomposites with NicalonTM and Hi-NicalonTM fibers and C and BN interphases versus the time to failure data from individual fibers at different temperatures. The rationale for this was that a composite, when the matrix is cracked, can only perform as well as the intrinsic or extrinsic fiber creep or rupture properties (numbers i and ii above). If the composite properties are worse than the fiber properties for the same load, the loss in load carrying ability is due to some composite degradation mechanism (numbers iii - v above). Data will be presented from previously published reports^{6,8} and from more recent experiments. The reasons for the

^{**} Nippon Carbon Co., Japan

differences in elevated temperature stressed-oxidation properties is discussed in light of the above mentioned mechanisms.

2. EXPERIMENTAL PROCEDURE

The processing^{6,9}, microstructure^{6,9}, and testing^{6,8} of the individual minicomposites have been described in detail elsewhere. In general, minicomposites were fabricated in two separate steps: (1) coating single fiber tows with $\sim 0.5 \mu\text{m}$ thickness C or BN and (2) composite fabrication with CVI SiC. The volume fraction of fibers for the minicomposites ranged from 0.1 to 0.2. The C coatings were applied via CVI in the same reactor as CVI SiC just prior to CVI SiC infiltration. The BN coatings were chemically vapor deposited with continuous-pull fiber tow coaters at $\sim 1050^\circ\text{C}$ ^{9,10} or 1400°C ^{9,11} and will be designated 3MBN and PBN, respectively⁹.

The minicomposites were first precracked in tension to a load which would insure matrix cracking along the entire gage length. The average matrix crack spacing was $\sim 1 \text{ mm}$. The elevated temperature tests were performed by gripping the samples outside of the furnace (cold gripped) and inserting a C-clamp furnace in the middle of the gage section. Minicomposite gage lengths ranged from 130 to 170 mm. The furnace was 35 mm long with a $\sim 12 \text{ mm}$ hot zone length. The furnace temperature profile was determined so that when minicomposites did not fail in the hot zone, the actual failure temperature of the minicomposite could be estimated. This is similar to the test approach prescribed by Heredia et al.¹².

3. RESULTS AND DISCUSSION

Typical constant load stress-rupture data for Nic-3MBN and Nic-C minicomposites are shown in Figure 1 and for HN-PBN and HN-C in Figure 2. The arrows in Figures 1 and 2 indicate the rupture sample did not fail. The HN-C minicomposites displayed a wide scatter in rupture stresses and times, this was not the case for the other minicomposites. The HN-C minicomposites were more spread out than the other minicomposites, almost having the appearance of loosely bonded individual microcomposites. This may have contributed to the scatter for this minicomposite system.

In order to compare individual fiber properties to minicomposite properties, all of the time-temperature data have been placed on a single Larson-Miller plot for specific fiber-type minicomposites. Yun and DiCarlo¹³ have demonstrated this approach with stress-rupture data^{14,15} for Nicalon and Hi-Nicalon fibers (Figure 3).

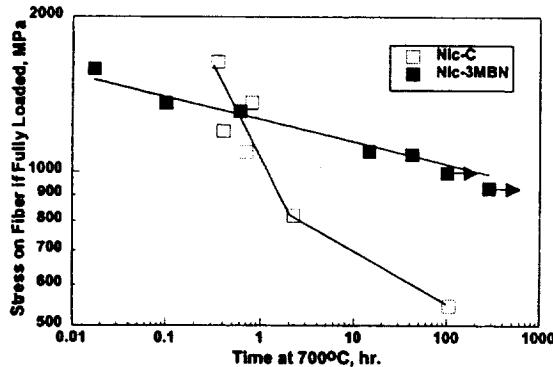


Figure 1: Typical stress rupture data for Nicalon minicomposites with C and 3MBN interphases at 700°C.

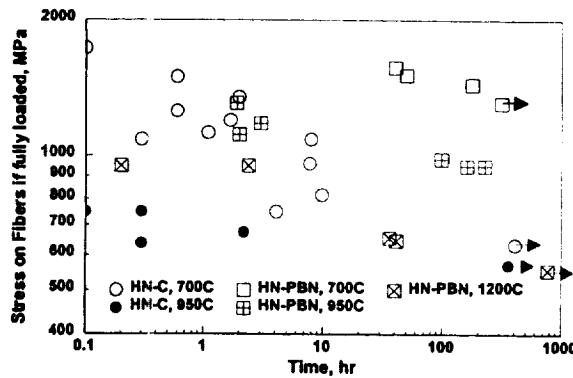


Figure 2: Typical stress rupture data for Hi-Nicalon minicomposites with C and PBN interphases at 700, 950, and 1200°C.

The curves were obtained by best-fitting stress-rupture, fast fracture, and warm-up test data¹³ with the Larson Miller parameter, q :

$$q = T (\log(t) + 22)$$

where T is temperature in K and t is time in hours. The Larson Miller constant was determined to be 22 for both fiber-types.

Larson Miller plots were used to compare the minicomposite and fiber data directly. Additionally rupture data has been normalized by the as-produced room temperature ultimate tensile stress. It was found that the as-produced composite strengths differed by as much as ~ 25% from lot to lot for the HN-BN system for different fiber batches and matrix runs. The high temperature strengths were also directly proportional to the room temperature ultimate strength for a given minicomposite set (see ref. 8).

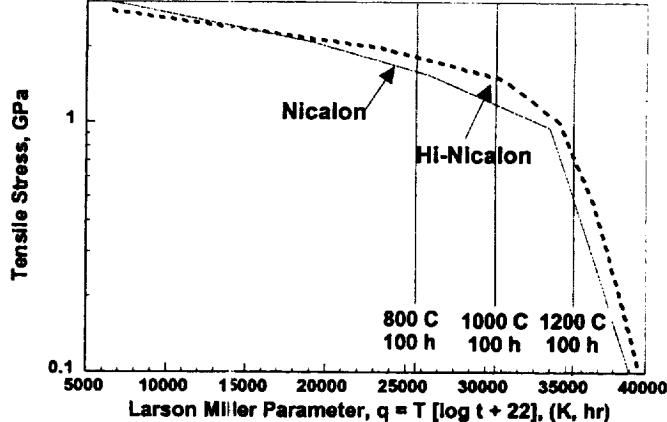


Figure 3: Larson-Miller plot for Nicalon and Hi-Nicalon fibers. The curves were determined from stress-rupture, fast fracture, and warm-up tests¹³.

Therefore, it was useful to normalize the high temperature rupture strengths by the room temperature ultimate strengths for each minicomposite batch. The Larson Miller plots for Nicalon and Hi-Nicalon minicomposites are shown in Figures 4 and 5 using this approach.

The most striking feature for both fiber-types was the difference in rupture behavior between the C-interphase and BN-interphase minicomposites. Both fiber-types exhibited similar rupture behavior with BN-interphases:

- (1) *at low temperatures* (< 700°C for Nic-3MBN and < ~ 900°C for HN-PBN) the minicomposite rupture behavior was the same as the individual fiber rupture behavior
- (2) *at intermediate temperatures* (700°C < T < 1000°C for Nic-3MBN and 900°C < T < 1050°C for HN-PBN) the minicomposite rupture properties were slightly worse than that of the individual fiber rupture properties
- (3) *at high temperatures* (> 1000°C for Nicalon and > 1050°C for Hi-Nicalon) the minicomposite rupture properties were similar to those of the individual fiber rupture properties.

Therefore, the minicomposite rupture behavior was fiber-controlled at low and high temperatures and at intermediate temperatures the minicomposite rupture behavior was controlled by some environmental degradation

mechanism(s). Fracture mirror analysis^{6,16} of the fibers which failed for the stress-rupture specimens in the intermediate temperature regime indicated that the fiber fracture stress decreased approximately the same amount as the decrease in failure load at rupture compared to the room temperature

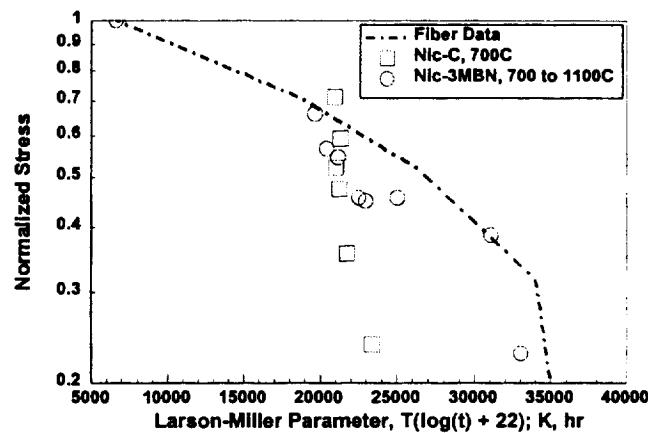


Figure 4: Larson-Miller plot for Nicalon minicomposites tested in stress-rupture.

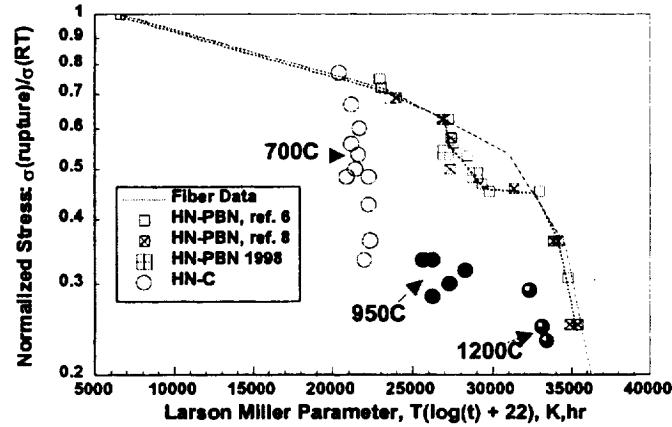


Figure 5: Larson-Miller plot for Hi-Nicalon minicomposites tested in stress-rupture.

fiber fracture stress and failure load, respectively. There was also some fiber-fusion to the matrix from the glass layer formed which was always the location of fiber failure at the rupture surface. Therefore, it was concluded that the mechanism causing stress-rupture at intermediate temperatures is a combination of fiber degradation and strong bonding due to the reactions of the interphase, fiber, and matrix with the environment. The reason why the intermediate temperature regime was at lower temperatures for the Nic-3MBN compared to HN-PBN may be due to the different BN interphases. The 3MBN was processed at a lower temperature and was therefore less resistant to oxidation than PBN¹⁷.

For the C-interphase minicomposites, a severe degradation in rupture properties occurs at 700°C. The Nic-C minicomposites were only tested at 700°C, however this same type of degradation (time dependence, e.g. Figure 1) has been observed in Nic-C macrocomposites for temperatures ranging from 425 to 1000°C^{3-4,18-20}. This is indicative of an environmentally controlled degradation mechanism. Fracture mirror analysis⁶ of the Nic-C minicomposite rupture surfaces indicated that the reduction in strength was due to a degradation in the strength of the fibers. The creation of large flaws sufficient to cause the strength reduction (which did not occur for as-produced fibers under similar stressed oxidation conditions) must be due to the alteration of the fiber surface from CVI SiC processing. Fracture mirror analysis has not yet been performed on the HN-C minicomposite rupture surfaces. However, the similar strength reduction at 700°C probably corresponds to the same type of fiber degradation mechanism. There does appear to be a "plateau" in rupture stress for the HN-C minicomposites at the higher temperatures which approached the fiber behavior at 1200°C.

Figure 6 shows the rupture (constant load) and cyclic load failure data for HN-C and HN-PBN minicomposites on a Larson-Miller plot. This plot is merely for comparative purposes, not mechanistic. The time to failure for the cyclic data was the actual time at temperature even though the peak load was less than that time. Two different fatigue conditions were performed: 0.01 hz loading cycles and a loading

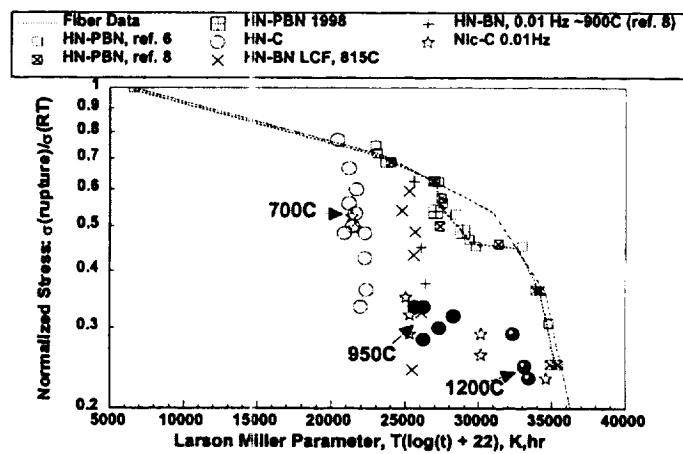


Figure 6: Stress-rupture and cyclic fatigue behavior of Hi-Nicalon minicomposites in air.

cycle where the load was held at the peak stress for two hours and then unloaded and reloaded to the peak stress (LCF). For the HN-PBN minicomposites, the cyclic behavior was significantly worse than the stress-rupture behavior at intermediate temperatures. For the HN-C minicomposites, the difference between cyclic and stress-rupture behavior was insignificant. This implies that HN-BN minicomposite stressed-oxidation behavior was more sensitive to the loading cycle; whereas, the HN-C minicomposite stressed-oxidation behavior was more sensitive to the exposure condition.

The hot zone of the furnace for the HN-PBN minicomposites which were subjected to 0.01 Hz⁸ was actually set at 1200°C. The failure location was always outside of the hot-zone at ~ 900°C. From fracture mirror analysis of the fibers which failed in cyclic loading for the HN-PBN minicomposites¹⁶ it was found that the fiber strengths were barely degraded even though the load-carrying ability of the lowest strength minicomposite was only ~ 25% of the original minicomposite strength. This indicated that the strength degrading mechanism for HN-PBN was not fiber degradation but strong bonding between the fiber and matrix which led to stress-concentrations on the fiber during cyclic loading. It is important to note that the degradation in HN-PBN properties under cyclic loading was slightly worse than that of HN-C minicomposites. The observance of poorer macrocomposites with BN interphases may or may not be observed depending on whether the onset of matrix cracking is less than or greater than the normalized stress condition where the HN-C and HN-PBN cyclic stress results intersect (Figure 6).

CONCLUSIONS

Stress-rupture and cyclic loading tensile tests were performed on Nicalon and Hi-Nicalon single tow CVI SiC minicomposites with C and BN interphases. All of the minicomposite systems displayed some degree of intermediate temperature strength degradation. For constant load conditions, the BN-interphase minicomposites outperformed the C-interphase systems. The HN-PBN system performed the best and the Nic-C system performed the worst. For cyclic load conditions, the degradation in load carrying ability for HN-PBN minicomposites was more severe than for stress-rupture conditions. However, the degradation in load carrying ability for HN-C minicomposites with cyclic loading was similar to stress-rupture conditions. In fact, for cyclic loading conditions, the strength-degradation of HN-PBN approached that of HN-C minicomposites.

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